

## The acid-base condition in vegetation, litter and humus: IX. Forms of bases.

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The »bases» (cations) present in plant materials occur in different forms of combinations which may be separated into the following groups:

1. Cations of soluble, organic and inorganic salts. These ions dialyze directly.
2. Cations in combination with acidoids. These cations can only be removed by exchange and may be dialyzed after the addition of ammonium salt.
3. Cations of insoluble precipitates such as calcium oxalate. These ions may be dialyzed after digestions with HCl.
4. Cations of the metal-organic compounds which do not dialyze.

The present paper is a report on a study of the distribution of the common cations (K, Mg, Ca, Mn) between these four forms of combinations in different plant materials. The investigation embraces also the distribution of phosphoric acid and silica.

### Description of materials.

The materials selected for the quadruple analysis include:

1. Fresh, undecomposed and unleached litter ( $F_0$  samples) from beech and ash in the Ultuna park (1943). The samples are from the same trees as the beech and ash leaves described in Part VIII of this series.

2. Six weeks old oat plants (tops only) from cylinder experiments (1943), including 12 differently fertilized samples.

3. Mature yellow pea plants (straw only) from cylinder experiments (1944), including 12 differently fertilized samples.

4. One hard-cooking and one soft-cooking sample of yellow peas.

The peas are not from the cylinder experiments but from samples supplied by professor R. Torssell in connection with an investigation of the cooking qualities of peas, the results of which will soon be published in *Acta Agriculturae Suecana*.

Our cylinder experiments are carried out in glazed terra cotta cylinders with an inside diameter of 30 cm and 85 cm in depth.

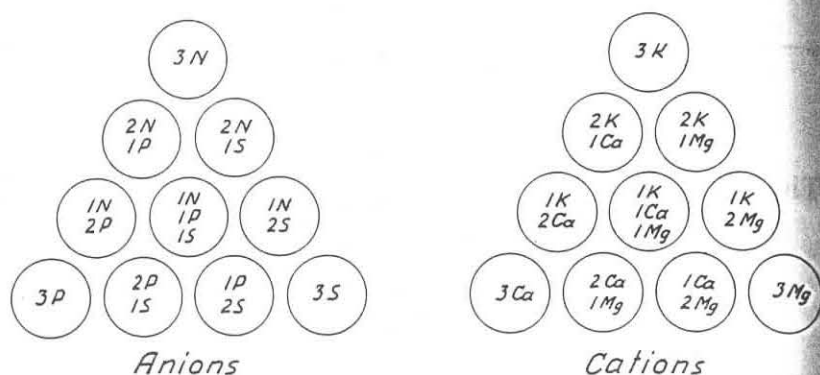


Fig. 56. Showing cylinder triangles. The anion cylinders receive the same amounts KCaMg, and the cation cylinders receive the same amounts NPS.

The experiment was started in 1942 when the cylinders were filled with a sandy soil taken from the trench in which they were placed. The cylinders are arranged in the form of two triangles: the «anion triangle» and the «cation triangle», each consisting of ten cylinders (fig. 56). Besides these triangle experiments there is a row of five cylinders representing special fertilizer treatment.

The fertilizer is added to each crop in the form of solutions which are made up and named as follows:

«Anion solutions»:

1. 3 N-solution: 400 m.mols  $\text{KNO}_3$ , 200 m.mols  $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{ aq.}$ , 200 m.mols  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{ aq.}$ , water q.s. 20 liters.
2. 3 P-solution: 400 m.mols  $\text{KH}_2\text{PO}_4$ , 200 m.mols  $\text{Mg}(\text{H}_2\text{PO}_4)_2$ , 200 m.mols  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 1 \text{ aq.}$ , water q.s. 20 liters.
3. 3 S-solution: 200 m.mols  $\text{K}_2\text{SO}_4$ , 200 m.mols  $\text{MgSO}_4 \cdot 7 \text{ aq.}$ , 200 m.mols  $\text{CaSO}_4 \cdot 2 \text{ aq.}$ , water q.s. 20 liters.

«Cation solutions»:

1. 3 K-solution: 400 m.mols  $\text{KNO}_3$ , 400 m.mols  $\text{KH}_2\text{PO}_4$ , 200 m.mols  $\text{K}_2\text{SO}_4$ , water q.s. 20 liters.
2. 3 Ca-solution: 200 m.mols  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{ aq.}$ , 200 m.mols  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 1 \text{ aq.}$ , 200 m.mols  $\text{CaSO}_4 \cdot 2 \text{ aq.}$ , water q.s. 20 liters.
3. 3 Mg-solution: 200 m.mols  $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{ aq.}$ , 200 m.mols  $\text{Mg}(\text{H}_2\text{PO}_4)_2$ , 200 m.mols  $\text{MgSO}_4 \cdot 7 \text{ aq.}$ , water q.s. 20 liters.

Each corner cylinder in a triangle receives 6 liters of a single solution (watered out in half liter portions during the first weeks of growth). The adjacent, two cylinders in the two sides of the triangle receive each 4 liters of the same solution. The next two cylinders in the same sides of the triangle and the cylinder in the center of the triangle receive each 2 liters of the same solution. In this way

each cylinder received 6 liters solution the composition of which is indicated in fig. 56.

The row cylinders were watered with the following solutions:

1.  $\text{NH}_4$  + metals solution: 120 m.mols  $(\text{NH}_4)_2\text{SO}_4$ , 120 m.mols  $\text{KH}_2\text{PO}_4$ , 30 m.mols  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 1 \text{ aq.}$ , 15 m.mols  $\text{Mg}(\text{H}_2\text{PO}_4)_2$ , water q.s. 6 liters.
2.  $\text{NH}_4$  - metals solution: 120 m.mols  $\text{NH}_4\text{H}_2\text{PO}_4$ , 60 m.mols  $(\text{NH}_4)_2\text{SO}_4$ , water q.s. 6 liters.
3. Alkali salt solution: 200 m.mols  $\text{KNO}_3$ , 200 m.mols  $\text{NaH}_2\text{PO}_4 \cdot 1 \text{ aq.}$ , 200 m.mols  $\text{Na}_2\text{SO}_4$ , 200 m.mols  $\text{NaCl}$ , water q.s. 6 liters.
4. Concentrated solution: 400 m.mols  $\text{KNO}_3$ , 200 m.mols  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 1 \text{ aq.}$ , 200 m.mols  $\text{MgSO}_4 \cdot 7 \text{ aq.}$ , water q.s. 6 liters.
5. Distilled water.

After application of the 6 liters of nutrient solution the plants are watered with distilled water when needed.

The experiment was started 1942 with a crop of barley, followed by oats in 1943, yellow peas in 1944 and potatoes in 1945. The quadruple analyses here dealt with include only the oat and pea crops, and is limited to the six corner cylinders of the triangles (3 N, 3 P, 3 S, 3 K, 3 Ca, 3 Mg), one of the two center cylinders and the five cylinders in the row.

Table 56 shows the yield of hay of the six weeks old oat plants, together with the yield of straw and kernel from the pea crop.

The oat was seeded on May 5th and was cut on June 18th before the appearance of ears. The 3 S-, the 3 P- and the water-plants showed the poorest development. The two  $\text{NH}_4$ -plants began to turn yellow at the tips of the leaves at the end of the period. The cation-plants looked the best.

The peas were seeded on May 24th and harvested in August between the 8th and the 19th. The anion-plants looked slightly poorer and were the first to ripen. The  $\text{NH}_4$  + metals-plants gave by far the greatest yield.

It is interesting to note that the pH, which was taken after the harvest of the pea crop in 1944, has already, after three applications of fertilizer, decreased by about 1.5 units in the  $\text{NH}_4$  + metals cylinder, which receives large applications of  $(\text{NH}_4)_2\text{SO}_4$ .

## Methods.

Thoroughly washed and electrodyalized cellophane tubing, 55 mm in width, is cut in 20 cm lengths. Five to ten grams of the finely ground plant material is placed in the middle of the tubing, and water or solution, together with a few drops of toluol, is added to cover the material. The two ends of the tubing are joined and folded once transversely about 8 to 10 mm from the ends. They are then folded once longitudinally, rolled up and fitted into a piece of rub-

Table 56. *The yield of oat hay (1943) and of yellow peas, straw and kernel (1944), from cylinder experiments (fig. 56). The pH of the soil was taken after three fertilizer treatments.*

Treatment	pH of soil Nov. 1944	Oat hay, yield per cylinder		Pea crop, yield per cylinder			
		n:o plants	g	Straw		Peas	
				n:o plants	g	number	g
3 N .....	6.30	74	41.1	30	49.1	197	42.7
3 P .....	6.02	69	32.5	30	45.8	255	55.1
3 S .....	6.00	71	30.8	30	47.2	229	50.0
3 K .....	6.20	75	53.6	30	65.2	294	64.1
3 Ca .....	6.12	74	47.0	30	84.3	361	90.5
3 Mg .....	6.32	74	47.9	29	64.3	276	61.7
KCaMg .....	6.23	74	50.7	30	63.0	276	61.2
NH <sub>4</sub> + metals	4.40	72	44.3	28	88.8	560	137.8
NH <sub>4</sub> - metals	4.98	68	33.7	23	53.8	311	72.7
Alkali .....	6.28	72	37.5	25	52.8	278	49.4
Conc. ....	6.28	74	52.7	30	76.5	308	73.7
H <sub>2</sub> O .....	5.96	69	28.4	30	49.2	256	51.7

ber tubing about 15 mm in length. A short piece of glass rod is now pushed up into the fold of the cellophane tubing, thus sealing up the bag which is now ready for dialysis. The bags are placed in tall, 250 cc beakers containing about 150 cc water. With the proper amount of air enclosed in the bags they can be made to float in the beakers at the desired degree of submersion. The beakers are placed in a large aluminum pot, partly filled with water and provided with an inner perforated bottom. The pot is placed on a hot plate and the temperature is regulated to between 55 and 60° C. This insures an efficient convection in the beakers and prevents fermentation.

The solution in the beakers is replaced once daily and is evaporated on a steambath in preparation for the analysis.

The dialysis is carried out in three successive steps: 1. in water, 2. in 0.25 n. NH<sub>4</sub>Cl solution and 3. in 0.05 n. HCl solution. The first NH<sub>4</sub>Cl addition, following the water extraction, was made with 1 n. solution and the first HCl addition, following the NH<sub>4</sub>Cl extraction, was made with 0.1 n. solution. Fourteen replacements, each with about 125 cc, were found to be sufficient to remove each group of ions except in the case of the HCl-soluble Ca in beech leaves, which required 18 replacements.

The evaporated dialysates were made up to a volume of 200 cc. Of this 100 cc were taken for the determination of SiO<sub>2</sub>, Ca and Mg. In aliquots of the remainder we determined K by the flame photometric method of Schuhknecht (1937), P according to Scheel (1936) by the photo-electric method, and Mn photo-electrically in

the form of permanganate. In the case of the water dialysate we determined the loss on ignition of the solid matter and the »excess base» in the ashes. The dialyzed residues were ignited and analyzed in the same manner. Table 57 gives the results obtained.

Table 57. *The content of Ca, Mg, K, Mn, P<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub> in three successive dialysates and in the nondialyzing residue of beech and ash litter (F<sub>0</sub>), of hard- (H) and soft- (S) cooking yellow peas, of oat hay and of pea straw (table 56).*

Sample	Per 100 grams dry matter								
	Ca	Mg	K	Mn	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	Dialyze- able organic matter	»Excess base»	
	m. e.	m. e.	m. e.	m. e.	mg	mg	g	Whole sample m. e.	Dialyze- able m. e.
I. Water-dialysates:									
Beech F <sub>0</sub> ...	11.4	14.0	13.8	.53	304	934	10.9	121	23
Ash F <sub>0</sub> ....	131.7	31.7	15.9	.05	324	280	26.3	241	139
Peas H .....	1.4	6.0	22.3	.01	263	19	10.6	—	—
Peas S .....	1.1	6.1	28.7	.01	729	18	11.4	—	—
<i>Oat hay:</i>									
3 N .....	41.2	26.7	161.4	.13	978	523	31.3	211	188
3 P .....	18.6	15.6	145.0	.26	2449	995	29.1	101	93
3 S .....	26.7	16.3	143.4	.28	1095	382	31.2	127	114
3 K .....	22.6	16.4	195.3	.13	2035	603	31.6	170	153
3 Ca .....	40.3	24.7	128.1	.08	1432	550	30.8	147	123
3 Mg .....	28.0	42.2	131.4	.12	1471	604	30.1	143	124
KCaMg .....	28.8	26.3	186.7	.26	1084	673	31.1	158	139
NH <sub>4</sub> + metals	17.4	13.6	173.5	.35	2725	962	29.6	72	64
NH <sub>4</sub> - metals	23.4	17.8	141.4	.34	2681	1185	30.0	49	39
Alkali .....	22.1	22.0	106.5	.60	1416	913	29.2	110	90
Conc. ....	28.7	34.9	471.2	.22	1657	1373	31.2	187	155
H <sub>2</sub> O .....	29.5	16.0	151.2	.34	1146	605	30.6	148	125
Average	27.3	22.7	177.9	.26	1681	781	30.5	135	117
<i>Pea straw:</i>									
3 N .....	115.1	48.4	67.2	.21	99	90	23.5	300	222
3 P .....	26.2	18.1	112.7	.14	2090	267	15.1	79	28
3 S .....	40.5	34.4	21.9	.21	165	126	17.7	166	104
3 K .....	27.9	11.7	93.5	.14	719	149	17.7	162	108
3 Ca .....	116.2	22.2	66.4	.25	457	191	20.2	155	101
3 Mg .....	58.2	84.7	37.5	.22	646	135	21.7	161	108
KCaMg .....	54.6	34.8	—	.14	662	160	16.8	170	106
NH <sub>4</sub> + metals	53.0	17.6	29.0	.37	505	214	15.4	120	67
NH <sub>4</sub> - metals	75.6	30.1	23.3	.75	418	213	16.6	135	43
Alkali .....	52.2	13.6	55.6	.19	435	87	15.2	133	71
Conc. ....	45.9	46.9	86.1	.09	784	173	24.4	184	131
H <sub>2</sub> O .....	68.4	27.7	54.5	.25	135	111	19.1	186	123
Average	61.2	32.5	58.9	.25	593	160	18.6	163	101

Sample	Per 100 grams dry matter					
	Ca m. e.	Mg m. e.	K m. e.	Mn m. e.	P <sub>2</sub> O <sub>5</sub> mg	SiO <sub>2</sub> mg
II. NH <sub>4</sub> Cl-dialysates:						
Beech F <sub>0</sub> .....	29.7	9.5	.9	.68	6	1128
Ash F <sub>0</sub> .....	60.9	6.2	.6	.00	44	46
Peas H.....	2.2	.5	.5	.01	83	10
Peas S.....	2.3	.6	.2	.02	159	13
<i>Oat hay:</i>						
3 N.....	11.1	3.3	2.2	.00	13	206
3 P.....	11.1	3.6	2.8	trace	40	556
3 S.....	8.2	2.7	2.4	»	6	224
3 K.....	8.3	3.2	3.4	.00	9	346
3 Ca.....	10.2	3.2	1.6	.00	21	239
3 Mg.....	8.7	5.1	1.5	trace	19	234
KCaMg.....	10.8	4.3	2.8	.00	13	244
NH <sub>4</sub> + metals .	11.0	3.5	2.5	trace	34	475
NH <sub>4</sub> - metals .	10.7	2.6	1.5	»	67	534
Alkali.....	10.1	3.4	1.6	»	34	389
Conc. ....	9.7	4.6	2.1	»	20	438
H <sub>2</sub> O.....	9.7	3.6	3.0	»	10	340
Average	10.0	3.6	2.3	trace	24	352
<i>Pea straw:</i>						
3 N.....	54.5	5.6	.8	.00	5	18
3 P.....	39.3	7.2	1.8	.00	136	20
3 S.....	32.1	8.7	2.2	.00	5	13
3 K.....	30.0	4.2	1.6	.00	8	18
3 Ca.....	36.5	2.5	.5	.00	20	15
3 Mg.....	29.4	13.1	.7	.00	18	11
KCaMg.....	36.0	6.8	1.5	.00	15	9
NH <sub>4</sub> + metals .	36.3	3.7	.9	.00	13	37
NH <sub>4</sub> - metals .	36.9	4.3	.7	.00	10	24
Alkali.....	35.9	2.4	1.5	.00	12	7
Conc. ....	32.2	8.4	2.3	.00	14	11
H <sub>2</sub> O.....	37.4	3.9	.7	.00	4	13
Average	36.4	5.9	1.3	.00	22	16
III. HCl-dialysates:						
Beech F <sub>0</sub> .....	56.4	.9	.6	.00	7	76
Ash F <sub>0</sub> .....	15.6	1.3	.5	.01	23	36
Peas H.....	1.1	.5	.1	.00	71	2
Peas S.....	.7	.5	.1	.00	64	2

Sample	Per 100 grams dry matter					
	Ca m. e.	Mg m. e.	K m. e.	Mn m. e.	P <sub>2</sub> O <sub>5</sub> mg	SiO <sub>2</sub> mg
<i>Oat hay:</i>						
3 N.....	2.2	.4	.6	trace	3	24
3 P.....	2.0	.7	.6	»	3	35
3 S.....	.8	.6	.5	.00	2	23
3 K.....	2.3	.4	.6	.00	5	12
3 Ca.....	2.5	.3	.6	trace	5	17
3 Mg.....	1.9	.5	.6	.00	5	24
KCaMg.....	.9	.8	.6	.00	3	6
NH <sub>4</sub> + metals .	1.7	.8	.6	trace	5	24
NH <sub>4</sub> - metals .	1.5	.8	.6	.00	12	24
Alkali.....	1.9	1.0	.6	trace	3	6
Conc. ....	2.1	.3	.6	.00	5	12
H <sub>2</sub> O.....	1.4	.8	.6	trace	2	0
Average	1.8	.6	.6	trace	4	17
<i>Pea straw:</i>						
3 N.....	17.2	.9	.4	.01	8	33
3 P.....	18.1	1.2	.4	.02	13	24
3 S.....	16.7	1.8	.4	.01	8	37
3 K.....	11.4	1.2	.4	.01	11	59
3 Ca.....	16.1	1.7	.4	.02	24	33
3 Mg.....	13.4	1.6	.4	.02	9	40
KCaMg.....	16.4	.8	.4	.01	12	18
NH <sub>4</sub> + metals .	15.0	1.1	.3	.01	9	42
NH <sub>4</sub> - metals .	16.9	1.0	.4	.01	8	29
Alkali.....	14.7	1.6	.3	.01	7	28
Conc. ....	12.0	1.3	.4	.00	9	46
H <sub>2</sub> O.....	20.0	.6	.4	.01	8	4
Average	15.7	1.2	.4	.01	10	33
IV. Dialyzed residues:						
Beech F <sub>0</sub> .....	7.9	.4	n. d.	.01	23	622
Ash F <sub>0</sub> .....	1.1	.4	»	.02	45	640
Peas H.....	.2	.2	»	.00	117	28
Peas S.....	.2	.1	»	.00	135	103
<i>Oat hay:</i>						
3 N.....	1.3	.6	n. d.	trace	26	541
3 P.....	1.9	.5	»	»	21	773
3 S.....	.6	.5	»	»	25	384
3 K.....	1.1	.6	»	»	22	538
3 Ca.....	2.0	.8	»	»	27	571
3 Mg.....	1.4	1.1	»	»	25	342
KCaMg.....	.4	.4	»	»	33	876
NH <sub>4</sub> + metals .	.9	.5	»	»	39	1176
NH <sub>4</sub> - metals .	.8	.4	»	.00	53	1243
Alkali.....	.2	.3	»	.00	34	671
Conc. ....	.4	.7	»	trace	32	912
H <sub>2</sub> O.....	.4	.2	»	.00	31	956
Average	1.0	.6	—	trace	31	749

Sample	Per 100 grams dry matter					
	Ca m. e.	Mg m. e.	K m. e.	Mn m. e.	P <sub>2</sub> O <sub>5</sub> mg	SiO <sub>2</sub> mg
<i>Pea straw:</i>						
3 N .....	.6	.4	n. d.	.01	9	454
3 P .....	.6	.3	»	.01	33	459
3 S .....	.3	.5	»	.00	11	320
3 K .....	.6	.2	.7	.01	16	342
3 Ca .....	.3	.2	n. d.	.00	18	196
3 Mg .....	.6	.4	»	.01	17	528
KCaMg .....	1.4	.5	.1	.02	16	252
NH <sub>4</sub> + metals ..	1.3	.6	n. d.	.01	20	557
NH <sub>4</sub> — metals ..	.2	.6	»	.01	17	485
Alkali .....	1.7	.7	»	.02	17	1062
Conc. ....	.3	.4	»	.00	15	147
H <sub>2</sub> O .....	.5	.4	»	.00	10	175
Average	.7	.4	—	.01	17	415

Sample	Ca	Mg	K <sup>1</sup>	Sample	Ca	Mg	K <sup>1</sup>
V. Total m. e./100 g:							
Beech F <sub>0</sub> ...	105.4	24.8	15.3	Pea straw...	114.0	40.0	60.6
Ash F <sub>0</sub> ....	209.3	39.6	17.0	Peas H .....	5.3	7.2	22.9
Oat hay ....	40.1	27.5	180.8	Peas S .....	4.4	7.3	29.0

VI. Percentage distribution:							
<i>H<sub>2</sub>O-dialysates:</i>							
Beech F <sub>0</sub> ...	10.8	56.5	90.2	Pea straw...	53.7	81.3	97.2
Ash F <sub>0</sub> ....	62.9	80.1	93.5	Peas H .....	26.4	83.3	97.3
Oat hay ....	68.1	82.5	98.4	Peas S .....	25.0	83.6	99.0
<i>NH<sub>4</sub>Cl-dialysates:</i>							
Beech F <sub>0</sub> ...	28.2	38.3	5.9	Pea straw...	31.9	14.8	2.1
Ash F <sub>0</sub> ....	29.1	15.7	3.5	Peas H .....	49.1	7.0	2.2
Oat hay ....	24.9	13.1	1.3	Peas S .....	52.3	8.2	.7
<i>HCl-dialysates:</i>							
Beech F <sub>0</sub> ...	53.5	3.6	3.9	Pea straw...	13.8	3.0	.2
Ash F <sub>0</sub> ....	7.5	3.3	2.9	Peas H .....	20.8	7.0	.5
Oat hay ....	4.5	2.2	.3	Peas S .....	15.9	6.8	.3
<i>Residues:</i>							
Beech F <sub>0</sub> ...	7.5	1.6	—	Pea straw...	.6	1.0	—
Ash F <sub>0</sub> ....	.5	1.0	—	Peas H .....	3.8	2.8	—
Oat hay ....	2.5	2.2	—	Peas S .....	6.8	1.4	—

<sup>1</sup> The K in the residues not included.

We shall begin our discussion of the results by considering the two kinds of litter, which show some very interesting differences.

In the water soluble fraction the ash leaves contain over eleven times as much Ca as the beech leaves but only a little more than double the amount of Mg and very little more K. The beech leaves contain ten times as much Mn as the ash leaves, about the same amount of P<sub>2</sub>O<sub>5</sub> but over three times the amount of SiO<sub>2</sub>. There is about two and a half times as much soluble organic matter in ash as in beech leaves, but this organic matter is associated with six times more «excess base» in the ash than in the beech leaves. Of total «excess base» there is however only twice as much in the ash as in the beech leaves. It is therefore already obvious that the bases must be differently distributed in the two kinds of litter.

In table II we find that the exchangeable (acidoid-bound) Ca shows the same proportion as the total «excess base», being twice as large in ash as in beech leaves. The exchangeable Mg is however 50 % greater in the beech than in the ash leaves. Since the soluble ions (in I) must be assumed to exist in a state of equilibrium with the exchangeable ions (in II) we can satisfactorily account for the observed relationships. The Ca ions, which have a greater displacing power than Mg, show a relative as well as absolute dominance over Mg in the exchangeable form, as compared to the soluble form of these ions. Despite the fact that there is more soluble Mg in ash than in beech leaves, there is more exchangeable Mg in beech than in ash leaves because in the beech leaves the soluble Ca is eleven times smaller than in the ash leaves and competes therefore less with the Mg ions in the exchange reaction.

There is very little K in the exchangeable form in all of the samples despite the fact that the amount of water-soluble K is often very large. But K, as a monovalent cation, must have suffered an extensive displacement, as an effect of dilution, during the water extraction (MATTSON 1942). The amount of K ions existing in the exchangeable condition in the original plant acidoids must have been considerable since K, in high concentrations, possesses a strong displacing power.

The SiO<sub>2</sub> is much higher in beech than in ash leaves, and the fact that the largest fraction of the silica in beech is released in the NH<sub>4</sub>Cl-dialysate indicates that it functions as an acidoid and binds some of the exchangeable divalent cations which, when displaced by NH<sub>4</sub>, render the silica soluble. The fact that silica binds Mg much more firmly than it binds Ca (as measured by displacement with NH<sub>4</sub>Cl) (JOFFE et al. 1935) might be a contributing cause to the relatively high amount of exchangeable Mg in the beech leaves.

In table III we find that no less than 56 m. e. Ca, or considerably more than half of the total Ca in the beech leaves, exists in



the insoluble and nonexchangeable but acid-soluble form. This accounts for the relatively low amount of Ca in the water- and  $\text{NH}_4\text{Cl}$ -dialysates and for the relative increase in exchangeable Mg.

This effect of oxalic acid as a Ca-precipitant must have far-reaching consequences for the living plant. Some of these will be discussed later.

The ash leaves, which yield large amounts of excess base in the water-dialysate, and which must therefore be assumed to contain large amounts of organic acids, contain much less precipitated, HCl-soluble Ca. The organic acids in ash leaves are predominantly of the kind forming relatively soluble Ca salts, such as citric, malic and others of the plant acid family.

The other ions in the HCl-dialysate are all present in small quantities and will be considered collectively later in connection with the other materials.

The compounds which we have called metal-organic are quantitatively of minor importance. The residues (table IV) contain only small amounts of mineral matter with the exception of  $\text{SiO}_2$  of which the beech and ash leaves still contain about 10 millimols/100 g. The appreciable amount of Ca in beech (7.9 m. e.) might in part be due to an incomplete solution of precipitated Ca by HCl.

The peas contain relatively small amounts of bases. Of these Ca exists chiefly in the exchangeable condition whereas most of the Mg together with K is water soluble. Ca is a little lower, K a little higher and, the most significant of all,  $\text{P}_2\text{O}_5$  is much higher in the soft- than in the hard-cooking peas. The relationship between these factors and the cooking qualities of peas will be discussed later.

If we now turn our attention to the oat hay and the pea straw and make a general comparison, we find that the straw contains, on the average, considerably more water soluble and exchangeable Ca and Mg, and very much more precipitated (oxalate) Ca than the oat hay, which is much richer in K,  $\text{P}_2\text{O}_5$  and  $\text{SiO}_2$ .

The average dialyzeable organic matter and its «excess base» are higher in the hay than in the mature straw as might be expected, but the average total amount of «excess base» is highest in the pea straw. The pea straw has a relatively very high acidoid content, higher even than the acidoid content of the young oat hay. (Examples from unpublished data: pea straw 57, oat hay 43, oat straw 20, all in m. e./100 grams electrodialyzed material.) This fact together with the high amount of oxalate-precipitated Ca in pea straw accounts for the relatively high «excess base» content of this material.

The influence of the different fertilizers shows itself in many ways in the water-dialysates:

The 3 N (nitrate) plants are very high in «excess base» and in divalent cations, but low in  $\text{P}_2\text{O}_5$ .

The 3 P plants are very high in  $\text{P}_2\text{O}_5$ , and the pea straw is also high in K, but both hay and straw are low in divalent cations. The «excess base» is low, as it always is, in the presence of much phosphate, especially when the ashes are titrated to phenolphthalein as done by us. A high  $\text{SiO}_2$  content seems to go with a high  $\text{P}_2\text{O}_5$ -content, possibly as a result of a displacement of silicate ions by phosphate in the soil.

The 3 S straw is very low in K and P, whereas Mg is relatively high.

The 3 K hay and straw are high in K and P but low in Ca and Mg.

The 3 Ca plants are very high in Ca, and the 3 Mg plants are very high in Mg.

The  $\text{NH}_4$  plants are all low in «excess base», but the up-take of the individual cations is very different in the two species of plants. Ca and Mg are both low in the oat hay whereas K is high. In the pea straw K is very low but Ca is high. The fact that Mn is high in all four of the  $\text{NH}_4$  samples is probably due to the low pH of the soil in these cylinders.

The «alkali» samples are both low in «excess base». The hay is low in Ca whereas the straw is low in Mg.

The «concentrated» samples show in general high figures for all the elements. In the hay the K is exceptionally high.

The  $\text{H}_2\text{O}$  samples are not particularly low in anything with the exception of  $\text{P}_2\text{O}_5$ . The soil is apparently able to supply sufficient amounts of the various cations without the addition of fertilizer.

The effects of the different cations, when supplied in excess, is in general agreement with the findings of plant physiologists (HOAGLAND 1944, LUNDEGÅRDH 1945).

The most outstanding result, from the point of view of the acid-base condition in plants, is the difference between the effects of the nitrate and ammonia nitrogen. This has also been observed by other workers. Thus CLARK (1936) found over twice as much organic acids in nitrate as in ammonium fertilized tomato plants. This would be equivalent to over twice as much «excess base» in the nitrate as compared to the ammonium plants. The high «excess base» content of nitrate plants must represent the base set free when the  $\text{NO}_3$  ion is assimilated. By a compensatory mechanism the plant synthesizes the organic acids necessary to neutralize the base. The process thus appears to be analogous to the autoxidation of humus, to organic acids and acidoids, which follows upon the addition of a base (MATTSON 1943).

It is of interest in this connection to mention that MATTSON and KARLSSON (1944) found a correlation between nitrogen and base content in native, brown earth and podzol vegetation.

Turning now to table 57, II we find the variations in composition

within the hay and straw series to be more regular and, where the variations are pronounced, more easy to trace. Thus both the 3 Mg hay and the 3 Mg straw, which are high in water soluble Mg, show a high proportion of exchangeable (acidoid-bound) Mg, and a somewhat suppressed amount of Ca.

There seems to be no such relationship between the »water soluble» and the exchangeable Ca. Only in the case of 3 N straw, which is high (115 m. e.) in water soluble Ca, do we find a correspondingly high value for exchangeable Ca. In 3 Ca hay and 3 Ca straw the exchangeable Ca does not exceed the average amounts. But now it is very probable that what we have extracted as water soluble Ca was only partly in solution in the original sap. Even plant acids other than oxalic, such as citric and malic, form sparingly soluble calcium salts. The Ca concentration in the sap of the 3 Ca plants might therefore not have been higher than in the other plants. It will all depend upon the nature of the organic acids in the plants, i.e., upon the solubility of their Ca salts. The acids in the 3 N plants might be different from the acids in the 3 Ca plants. CLARK (1936) found the acids in the nitrate and the ammonium tomato plants to be radically different.

We should here like to quote HOAGLAND (1944) where he discusses his cylinder experiments with prune trees. He writes: »While the potassium deficient trees usually contained in their leaves a higher percentage of total calcium and magnesium than was found in the trees receiving an adequate supply of potassium, hardly any of the calcium was present in dissolved form (in the expressed sap) and only part of the magnesium.»

If the cell sap is saturated with respect to an organic salt, no increment in the total amount of cations of that salt can increase their concentration in the sap as long as the plant produces an equivalent amount of the corresponding acid. If the concentration in the sap remains unaltered, the composition of the exchangeable cations will also remain unaltered. The importance of this for the constitution and functions of the protoplasm, its charge, its solvation, its permeability etc., is readily perceived when we recall the powerful effect exerted by changes in the proportions of mono- and divalent cations on the properties of negative colloids. Some of the special functions of the sparingly soluble salts will be discussed later.

Returning to table II we note that there is, on the average, over three times as much exchangeable Ca in pea straw as in oat hay, but less than twice the amount of exchangeable Mg. The average ratio of exchangeable Ca/Mg is 2.77 in the hay and 6.17 in the straw. Here again it must be emphasized that the composition of the exchangeable cations must have undergone changes during the leaching with water, resulting in a loss of K and a gain in Ca and Mg.

The HCl-dialysate (table III) shows fairly large amounts of Ca in the pea straw. The quantities vary between 11.4 m. e. in the 3 K sample and 20.0 m. e. in the H<sub>2</sub>O sample. In oat hay the quantities of Ca are much smaller (0.8 to 2.5 m. e./100 g).

The question arises whether this difference in the content of precipitated, HCl-soluble Ca in oat hay and pea straw is wholly specific in character or if it is also the result of a difference in maturity.

In our previous paper in this series we found indications (Part VIII, table 51 a), in the case of some of the leaves (beech, oak and pine), of an increase in the amount of precipitated base with the age of the leaves. The »excess base» in the water soluble fraction decreased, in these samples, with the maturity of the leaves, whereas the »excess base» in the insoluble residue increased much faster than the increase in the acidoid content.

Another question of interest to the pedologist is the question of the resistance to decomposition of calcium oxalate in neutral and acid soils. To what extent does oxalic acid contribute to the podzolization process?

In order to find an answer to these questions we subjected a number of plant materials of different maturity, and neutral and acid beech-leaf humus to a thorough leaching with 1 n. solution of NH<sub>4</sub>Cl. When the filtrate was free from Ca ions we digested the residue over night with 0.5 n. HCl and then leached with 0.05 n. HCl until the filtrate was again free from Ca ions. The Ca in the HCl extracts was then determined. The results are shown in table 58.

Among these materials there are five samples of spruce needles, all from the same tree and representing the last five seasons of growth. The needles were collected in August 1941 from a 40 year old spruce in Båstad. The soil is a fertile rendzina.

The oat hay and straw samples are from our cylinder experiments 1943. The leaves from the Ultuna park are from the same trees as the 1941 samples described in Part VIII of this series. The V<sub>1</sub> samples were collected in the early summer of 1943 as soon as the leaves were fully developed. The F<sub>0</sub> samples are from the autumn of the same year. The Axelstorp podzol F<sub>3</sub> sample is the same beech mold described in Part VIII. The Hallandsås F<sub>0</sub> sample of beech leaves and the same material after one year of aerobic and anaerobic decomposition are the same as the materials described in Part I of this series.

Table 58 shows 1. that the oxalate precipitated Ca increases greatly with the age of the leaves, 2. that the beech leaves from the acid soil contain less Ca-oxalate than the leaves from the neutral soil, 3. that the oxalate is decomposed both aerobically and anaerobically, 4. that there is very little oxalate Ca left in the beech-leaf mold, 5. that the spruce needles precipitate increasing amounts

Table 58. *The content of Ca, insoluble in water and in  $NH_4Cl$  solution but soluble in  $HCl$  solution (precipitated, oxalate calcium) in young and old plant materials.*

Sample		Ca m. e./100 g
Beech leaves	V <sub>1</sub> (Ultuna park, neutral soil) .....	25.9
»	F <sub>0</sub> ( » » » » ) .....	56.4 <sup>1</sup>
Ash	V <sub>1</sub> ( » » » » ) .....	5.4
»	F <sub>0</sub> ( » » » » ) .....	15.6 <sup>1</sup>
Pine needles	V <sub>1</sub> ( » » » » ) .....	1.6
»	F <sub>0</sub> ( » » » » ) .....	8.9
Beech leaves	F <sub>0</sub> (Hallandsås, acid soil) .....	30.0
»	» after 1 year aerobic decomposition .....	5.5
»	» » 1 » anaerobic » .....	8.0
Axelstorp beech-leaf mold (podzol F <sub>3</sub> humus) .....		1.1
Spruce needles, 3 months old (neutral soil) .....		11.8
» » , 1 year ( » » ) .....		24.6
» » , 2 » ( » » ) .....		41.6
» » , 3 » ( » » ) .....		56.4
» » , 4 » ( » » ) .....		76.0
Oat hay, cut July 2 (cylinder experiments) .....		.71
» straw, » Aug. 14 ( » » ) .....		.71

of Ca from year to year, and 6. that oat contains very little Ca-oxalate in both young and old plants.

The decomposition of the beech-leaf oxalate is greater than indicated in the table because a considerable amount of the leaves had also been decomposed, and the per cent is here expressed on the basis of the dry weight of the residues.

The fact that the beech leaves from the neutral soil contain more oxalate than the leaves from the acid soil might indicate that the production of oxalic acid takes place in response to a high Ca ion content.

In view of the great solvent action of oxalic acid on the sesquioxides one wonders to what extent, if any, this acid participates in the process of podzolization before it suffers decomposition. Beech and spruce are known to be active podzolizers.

We give here in table 59 the results of a study of the acid-base condition of the spruce needles. The acid-base condition of the other materials in table 58 has already been reported (MATTSON & ANDERSSON 1943, 1944). The method is here the same.

We note that the «excess base» increases from 33.0 m. e./100 g in the youngest to 112.9 m. e./100 g in the oldest needles. The ash content, the  $pH_0$ , the acids and acidoids and the base status (per cent base saturation) all increase in the same direction, while the acidity, the  $pH_u$  (pH of the electrodyalyzed material) and the nitro-

<sup>1</sup> From table 57, III.

gen content increase in the opposite direction to that of «excess base». Most of the four years of increase in «excess base» is accounted for by the simultaneous increase in precipitated Ca (table 58).

This withdrawal of Ca from the cell sap solution must be of great importance for the physiological functions of the plant colloids. The precipitation of Ca will cause a shift in the equilibrium between the dissolved cations and the exchangeable, acidoid-bound cations. The removal of Ca from active participation in this equilibrium

Table 59. *The acid-base condition in spruce needles from the same tree but of different maturity.*

Age of needles	Ash %	$pH_0$	M. e./100 g				Base status $\frac{B \times 100}{B+H}$	$pH_u$	N %
			«Ex- cess base» B	Acid- ity H	Acidoids (at pH 7.0) A	Acids. B+H -A= a			
3 months	3.11	3.51	33.0	67.6	28.0	72.6	32.8	3.31	1.73
1 year ...	4.02	3.69	55.4	68.2	34.5	89.1	44.8	3.20	1.67
2 years ..	4.65	3.72	66.8	57.2	32.5	91.5	53.9	3.18	1.43
3 years ..	5.76	3.93	86.2	48.8	35.0	100.0	63.9	3.05	1.32
4 years ..	7.29	4.06	112.9	43.3	39.5	116.7	72.3	2.87	1.26

leads to a higher proportion of Mg and monovalent cations in the exchange complex and this will tend to increase the eletrokinetic potential, the solvation, the viscosity and the swelling of the colloids. The removal of a salt from solution by precipitation will maintain a higher Donnan potential between the micellar solution and the free sap solution. The Ca ions powerfully suppress the activity of electronegative colloids. A removal of an «excess» of Ca by precipitation as oxalate might therefore be looked upon as a regulatory mechanism for the normal functions of protoplasm in many plants.

The production of oxalic acid and the precipitation of oxalates might also serve another purpose. Most of the rare earth metals are toxic to plants in very low concentrations (ROBINSON and EDINGTON, 1945). These metals all form slightly soluble oxalates. In plants which produce oxalic acid the ions of these metals can never reach a concentration higher than that which corresponds to the solubility product of their oxalates.

There are other *Ca-precipitants* in plants which are of importance as regulators (buffers) of the Ca ion concentration in the sap and of the proportion of the exchangeable Ca in combination with the plant acidoids. A precipitation which has its threshold just below the pH prevailing in the sap must be assumed to fulfill a very



important function, because a small change in pH might cause a large change in the balance between the active ions, mono- and divalent.

We shall now give an example of how such precipitants influence the character of plant colloids, and how the behavior of the latter depends upon the form of the plant bases.

We have seen that the soft-cooking peas contained less Ca but more K and P than the hard-cooking peas. Extracting with 2% HCl and analyzing for inorganic P, total P, organic P (by difference) and phytin P (according to HARRIS and MOSHER 1934), we found the following composition of the two samples of peas in mg P<sub>2</sub>O<sub>5</sub> per 100 g dry matter:

	Total	Inorganic	Organic	Phytin
Peas H.....	380	100	280	153
Peas S.....	954	150	804	597

We note 1. that most of the P is organic, 2. that most of the latter is in the form of phytin (inositol hexaphosphoric acid) and 3. that the soft-cooking peas contain nearly four times as much phytin as the hard-cooking peas.

By cooking experiments we have found:

1. that the hard-cooking peas can be made soft-cooking by the addition of ammonium oxalate, Na<sub>2</sub>CO<sub>3</sub> or NaOH to the water;
2. that the soft-cooking peas become hard-cooking if CaCl<sub>2</sub> is added to the water;
3. that if soaked in water (in the presence of toluol) for as long as one week all peas become entirely uncookable;
4. that if the peas are boiled for 10 minutes (after swelling in water for 4 hours) the soaking will have no effect, but leave the peas as cookable as in their original condition;
5. that Ca- and Mg-saturated peas are uncookable but that Na-saturated peas are extremely soft-cooking;
6. that Ca-saturated peas (and all other peas) become extremely soft-cooking if allowed to swell in a solution of Na-phytinate.

This, briefly stated, points to a colloid-chemical and bio-chemical mechanism. The valence of the exchangeable cations in combination with the pea acidoids govern the cooking qualities of the peas. But the proportion of the exchangeable mono- and divalent cations is governed by their relative concentration in the solution, and this is, for a given content of ions, in turn governed by the quantity of calcium precipitant present in the peas. The Ca-precipitant is apparently destroyed by an enzyme which in turn is destroyed by heat.

The Ca-precipitant in the peas is phytin and the enzyme is phytase.

When peas are soaked several days in water the phytin is hydro-

lyzed by phytase, yielding inorganic phosphates and inositol (the hydrolysis is much more rapid if the seed is ground to flour). The phosphoric acid is also a Ca (and Mg)-precipitant but requires higher pH than phytin. The hydrolysis of the phytin means, therefore, a higher Ca and Mg ion concentration in the solution, and this in turn means a high proportion of exchangeable Ca and Mg in combination with the pea acidoids. Such peas have always been found to be uncookable.

A sample of soft-cooking peas contained 56 mg inorganic P<sub>2</sub>O<sub>5</sub> and 580 mg organic P<sub>2</sub>O<sub>5</sub> of which 326 mg were in the form of phytin, all per 100 g peas. After soaking the peas in water for 8 days at 40° C the analysis showed 446 mg inorganic P<sub>2</sub>O<sub>5</sub> and 212 mg organic P<sub>2</sub>O<sub>5</sub>, of which only 47 mg were phytin. The peas were now uncookable. The addition of sufficient Na-phytinate to such peas (and all other peas examined) makes them very soft-cooking.

Fig. 57 shows the per cent cooked of the hard-cooking and the soft-cooking peas (in table 57) as a function of the pH. 50 g of peas were soaked for 18 hours in 200 cc of water to which HCl or NaOH were added to adjust the pH. The soft-cooking peas were boiled for 1 hour and the hard-cooking were boiled for 1 1/2 hour. The per cent of cooked peas was determined by the method of TORSELL (1942). The pH was determined in the juice of the cooked peas.

The experiment yields two characteristic U-curves whose minima lie between pH 4 and 5. The curve of the hard-cooking (H) peas occupies, however, a decidedly higher position on the pH scale than that of the soft-cooking (S) peas. The former are therefore, at their original pH (6.20) much nearer the point of minimum cookability than the latter at their original pH (6.10).

Since the curves are very steep in the region of the original pH of the peas, a small change in reaction will greatly affect the cookability. Hard-cooking peas can be made soft-cooking by raising the pH while soft-cooking peas become hard-cooking if the pH is lowered. The difference between the H-peas and the S-peas, from the point of view of cookability, is only a matter of a few tenths of a pH unit.

The form of the curves suggest that the cookability is related to the properties of the amphoteric proteins (the legumin) of the peas. The isoelectric point of the alkali-extracted, impure legumin was found to be about 4.4, which corresponds to the minima in cookability. Since the legumin is coagulated at, and for some distance on either side of the isoelectric point we might, like RITTHAUSEN (1872), conclude that the cookability of the peas is intimately related to the solubility of the legumin.

But there are several facts which do not fit in with this simple explanation: 1. In the presence of Na-oxalate the peas are easily

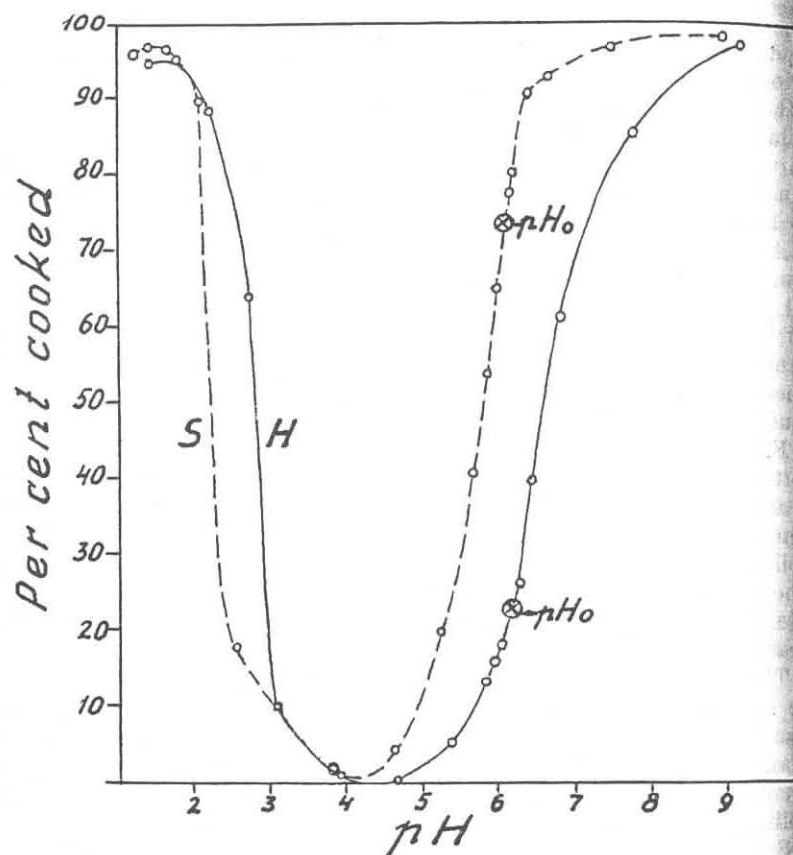


Fig. 57. Showing the cooking of hard-(H) and soft-(S) cooking peas as a function of pH. The H-peas were boiled 90 minutes and the S-peas 60 minutes.  $pH_0$  = pH of juice from peas to which neither HCL nor NaOH had been added.

cookable at all pH. 2. Na-oxalate does not prevent the coagulation of the legumin at the isoelectric point. 3. H-saturated peas (acetic acid extracted) and Na-saturated peas (NaCl-treated) cook easily at all pH. 4. It is only the untreated peas or peas saturated with Ca or Mg ions which yield the characteristic minima in cookability shown in fig. 57.

The isoelectric coagulation of the legumin has apparently nothing to do with the minimum in cookability, despite the coincidence of the two phenomena. The minimum in cookability is obviously conditioned by a high degree of saturation of the pea acidoids with divalent cations. The acidoids involved are not the weak protein acidoids inside the cells but the stronger pectic, possibly also other

polyuronic acidoids of the middle lamella which, saturated with divalent cations, form the cementing material between the cells.

Since the pectins, and the polyuronides in general, are not amphoteric it remains to explain the minimum in cookability (the false isoelectric point) between pH 4 and 5, and the ease with which the peas are cooked at lower as well as at higher pH.

If the cooking of peas depends only on the solvation of the pectin which, in the Ca and Mg saturated condition, binds the cells together, a study of the behavior of a material rich in pectin and poor in protein ought to yield useful information. For this purpose grape fruit albedo (the white portion of the rind) was saturated with Ca and with Na ions by repeated treatments with the respective chlorides. The Ca-saturated product was leathery and did not swell, whereas the Na-saturated swelled enormously even before the salt was removed by leaching. Portions of 0.1 gram of the dried samples were heated in 20 cc solution for 30 minutes at 70° C at various pH (adjusted by HCl or NaOH) with and without Na-phytate. The relative viscosity of the filtered solutions was then measured at 20° C by the Ostwald viscosimeter. The results are shown graphically in fig. 58.

The Ca-saturated albedo yields a viscous solution of pectin below pH 3.5. At higher pH it is insoluble if no Ca-precipitant is added. The addition of Na-phytate equivalent to 0.4 millimols  $PO_4$  per 0.1 gram albedo yields a U-curve showing a minimum viscosity about a pH of 5. This minimum in the solubility of the citrus pectin in the presence of Na-phytate corresponds therefore closely to the minimum in cookability of the peas.

The Na-saturated albedo had apparently lost pectin during its preparation for it yielded solutions of relatively low viscosities, with  $\eta_1/\eta_0$  values from 1.50 to 1.58 between pH 1.72 and 5.72. But there was no minimum as in the case of the Ca-albedo.

The experiment allows us to draw the following conclusion:

At low pH the Ca-pectinate is dissolved by the HCl and converted into soluble H-pectinate. At high pH in the presence of Na-phytate, Ca-phytinate is precipitated and the pectin is converted into soluble Na-pectinate.

These reactions are graphically shown in fig. 59.

The curves on the left side show the percent of the total Ca which was dissolved when 2.5 gram portions of Ca-saturated grape fruit albedo and 5 gram portions of Ca-saturated peas were extracted with 200 cc HCl solutions containing increasing amounts of acid. The total amount of exchangeable Ca was 48.50 m. e./100 g in the albedo, and 15.69 m. e./100 g in the peas. (Note that the two materials become desaturated with Ca within the same range of pH, indicating that their acidoids are of the same strength. Legumin gives off its Ca at much higher pH.)

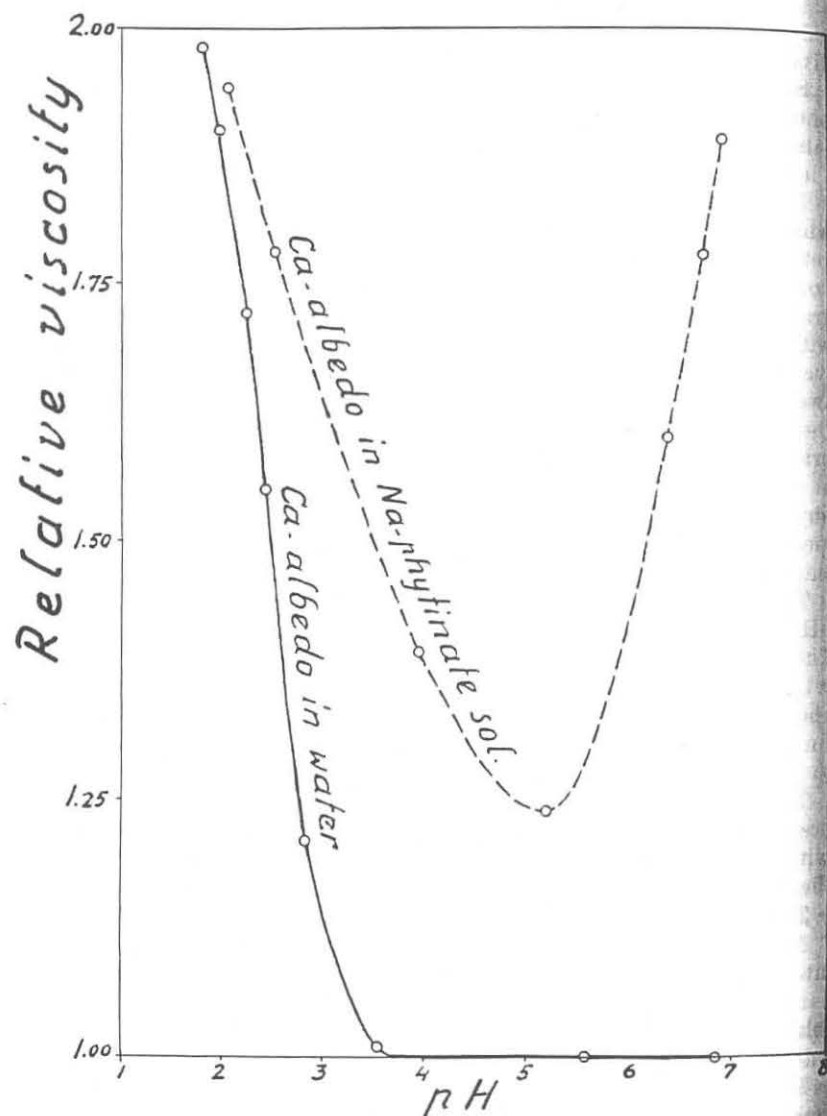


Fig. 58. Showing the relative viscosity of solutions obtained by heating Ca-saturated grape fruit albedo (white portion of rind) for 30 minutes at 70° C. The pH was adjusted by the addition of HCl or NaOH. The Ca-albedo was heated with and without Na-phytate.

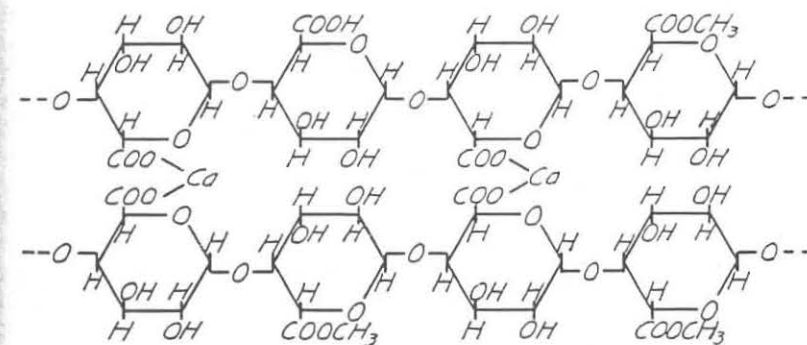
The curves on the right side in fig. 59 show the percent of Ca precipitated when NaOH was added to an acidified solution containing 4 m.e.  $\text{CaCl}_2$  together with Na-phytate equivalent to 2

millimols  $\text{PO}_4$  in 200 cc. Since Ca-phytate is more insoluble, and is precipitated at lower pH in a hot than in a cold solution the experiment was carried out both at 100° and at 20° C.

We note that the intersection of the two pair of curves occur between pH 4.75 and 5, or at pH values which closely correspond to the minimum in viscosity of the filtrate from the Ca-saturated albedo in the presence of phytate (fig. 58) and to the minimum in cookability of the peas (fig. 57). This minimum corresponds to a maximum in the Ca-pectinate content.

According to MYERS and BAKER (1934) unhydrolyzed pectin is monoarabino-monogalacto-diacetyl-heptamethoxyl-octagalacturonic acid. In Ca-pectinate the galacturonic chains are linked together by the divalent Ca ions which, according to BONNER (1936), are shared by carboxyl groups belonging to different molecular chains.

This cross linkage is pictured by BAKER and GOODWIN (1941) by the structure:



Pectin, which is a highly hydrophilic colloid, is very soluble when saturated with monovalent cations.

Fig. 59 thus explains the role of both pectin and phytin, and accounts for the behavior of peas with respect to their cooking qualities. The pectin exists in equilibrium with all the free cations in the solution. If the phytin content is low, more of the Ca will combine with the pectin and the peas will be hard-cooking. A high phytin content will precipitate a greater amount of the divalent cations, Ca and Mg, and leave the pectin in combination with an equivalent quantity of monovalent cations. This makes the peas soft-cooking.

Fig. 58 shows that the Ca-saturated citrus pectin begins to dissolve at pH 3.5. According to fig. 59 the pectin has lost 42 % of its Ca at this pH and is thus saturated with H ions to the extent of 42 % when it begins to dissolve.

The addition of Na-phytate (fig. 58) increases the solubility of

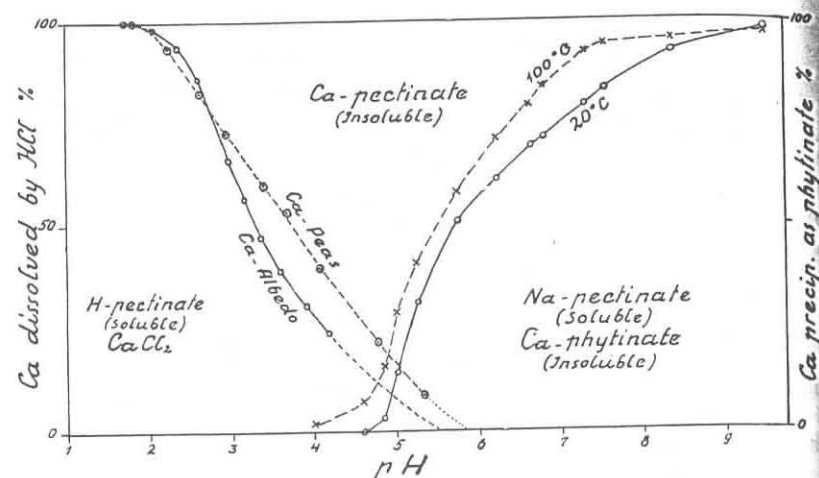


Fig. 59. Showing the solution of Ca from Ca-saturated albedo (fig. 58) and peas (curves on left), and the precipitation of Ca as phytinate (at 20° and 100° C) in a system containing 4 m. e.  $\text{CaCl}_2$  and an equivalent amount of Na-phytinate in 200 cc (curves on right). pH adjusted with HCl or NaOH.

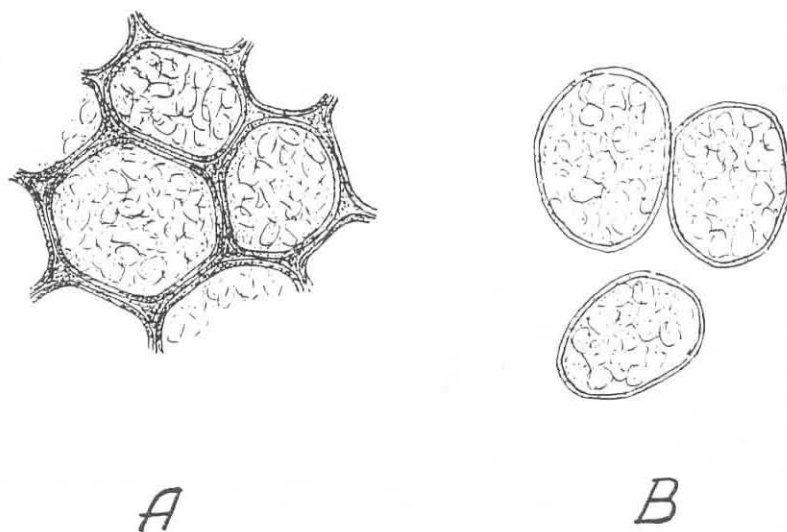


Fig. 60. A. Showing the appearance of cells of uncooked peas or of boiled but uncookable Ca-saturated peas. Middle lamella and cell walls stained deep blue with methylene blue.

Fig. 60 B. Cells of Na-saturated, cooked peas. The middle lamella has dissolved away but the cell walls are unruptured and the cells are still filled with aleurum grains and starch. Cells do not stain.

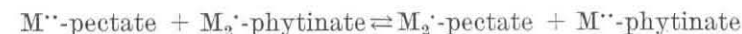
the pectin not only at high pH, where it acts as a Ca-precipitant, but extends its solvent action over on the acid side of the minimum. This must be due to a partial displacement of Ca by the Na ions. Even NaCl will produce this effect. This displacement of divalent by monovalent cations is still more evident in the Mg-saturated samples. Mg is less active than Ca and its effects are more easily suppressed. Thus although Mg-phytinate requires somewhat higher pH than Ca-phytinate for its precipitation, Mg-saturated peas are more affected and yield more narrow minima in cookability upon the addition of Na-phytinate.

The colloid chemical mechanism of the cooking of peas, which is graphically illustrated in fig. 59, may be studied in the microscope.

When thin slices of uncooked peas are examined in the microscope the cell walls and lamella show the somewhat hexagonal structure represented in fig. 60 A. The cells are filled with starch and aleurum grains. If the cells are treated with methylene blue (a basic dye which combines by exchange with the acidoids, MATTSON 1942) the cell walls and the lamella are stained deep blue. The contents of the cells are only faintly stained. If the peas are Ca-saturated, and therefore uncookable, they show the same structure and the same staining even after prolonged boiling. If the peas are Na-saturated, a few minutes of heating will cause the lamella to swell and dissolve and the cells to fall apart. The unruptured cells, which are now oval-shaped and thin-walled, are still filled with aleurum grains (fig. 60 B). The legumin still forms a part of the cell content. But the pectin of the middle lamella has been dissolved away. Even the pectin of the cell wall must have dissolved because the membranes do not now stain any deeper than the contents of the cell.

### Concluding remarks.

These experiments illustrate in a striking way the importance of the form in which the bases occur in plants. The peas do not contain much Ca or Mg, yet a small shift in the equilibrium



makes all the difference between hard-cooking and soft-cooking peas. An increase in the proportion of monovalent cations in combination with the hydrophilic colloid increases the charge and the solvation of the latter. An increase in the proportion of the divalent cations has the opposite effect, making the colloid less active and its structure more stable. The state of the colloid thus depends on the nature, the activity and the proportion of the cations.



By the synthesis of certain cation precipitants, possibly by a mechanism of metabolic response, the protoplasm possesses, within certain limits, the power to regulate the proportion of the cations. The production of oxalic acid permanently removes Ca. But the production of a precipitant like phytin, whose precipitation threshold lies just below the pH of the sap, supplies the cell with a very sensitive buffer system for the ions precipitated as well as for the hydrogen ions. An increase in pH will cause the removal of divalent cations from active participation in the exchange equilibrium, while a lowering of the pH will cause the release of such ions. This must have a profound effect on the electronegative protoplasmic colloids. A high pH and a high proportion of monovalent cations may be assumed to solvate the protoplasm and increase its metabolic activity, including the production of organic acids. A low pH and a high proportion of divalent cations may be expected to have the opposite effect and slow down the production of acids.

Whether or not there is anything in this speculation as to the regulation of the hydrogen ion activity, the constancy of which postulates some such mechanism, it seems obvious that the production of active «cation-precipitant-buffers», such as phytin and others, must be of great importance for the stability of the intricate structures and for the complex functions of the protoplasmic colloids, all of which largely depend on ionic exchange.

### Summary.

Litter of beech and ash leaves, oat hay and pea straw (from cylinder experiments with different fertilizers) and samples of hard-cooking and soft-cooking yellow peas were completely dialyzed through cellophane membranes, first in water, then in  $\text{NH}_4\text{Cl}$  solution, and finally in  $\text{HCl}$  solution.

The dialysates and residues were analyzed for Ca, Mg, Mn, K,  $\text{P}_2\text{O}_5$  and  $\text{SiO}_2$ .

The results show that a large proportion of the divalent cations, mostly Ca, exists in combination with the plant acidoids and is removable only by exchange.

The beech leaves, the ash leaves and the pea straw contained large to moderate amounts of oxalate-precipitated (acid-soluble) Ca. The oxalate increases with the maturity of the material as shown, among other things, by five seasons growth of spruce needles.

As in the case of electronegative colloids in general, the state and behavior of plant colloids depend on the nature and proportions of the active cations. Thus Ca-saturated peas are uncookable while Na-saturated peas are extremely soft-cooking.

There is present in plants certain Ca-precipitants whose precipitation threshold lies just below the pH of the sap. Such precipitants

act as buffers for the ions precipitated and regulate their activity in the sap and in the colloids. Inositol hexaphosphoric acid (phytin) is such a precipitant.

All hard-cooking peas become soft-cooking if allowed to swell in a solution of Na-phytinate. Soft-cooking peas possess a high phytin content.

The acidoid, which in the Ca-saturated condition makes the peas uncookable, is the pectin (a polyuronic acidoid) of the middle lamella. In the Na-saturated condition this pectin swells and dissolves in hot water, causing the unruptured cells to fall apart.

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